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Effect of Wood Species on Corrosivity of Black Liquors

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ABSTRACT

The corrosion rate of carbon and stainless steel equipment, like digesters, black liquor storage tanks, and other equipment that comes in contact with black liquor, varies from one mill to another and sometimes within the same mill. Generally, corrosivity of black liquor is known to change with the wood species pulped. Corrosivity of black liquor does not correlate with their inorganic constituents. Pulping conditions vary from mill to mill, leaving different amounts of residual inorganics, solids content, etc., in resulting black liquors. Therefore, it is difficult to evaluate the effect of organic constituents of black liquor on its overall corrosivity. The present study focuses on establishing relative corrosion susceptibility of carbon steels and other alloys in black liquors from different wood species which were pulped under similar cooking conditions, leaving similar amounts of residual inorganic chemicals in the resulting black liquors. Five different wood species (two softwoods and three hardwoods) were used in this study. Results from this study show that the tested black liquors from softwood species are more corrosive than the black liquors from the hardwoods tested. However, the corrosivity of black liquors from hardwoods depend upon the wood species used. No correlation was found between the major inorganic constituents of the black liquor and the corrosion rate of steel alloys in these liquors. This study clearly demonstrates the important role of organic constituents of black liquor in determining their corrosivity.

Keywords: Black liquor, corrosivity, softwood, hardwood, digester, wood extractives, organic constituents, inorganic constituents, wood species

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INTRODUCTION

The corrosion rate of kraft digesters and other equipment that come in contact with black liquor varies considerably. Black liquor consists of residual inorganic chemicals after pulping, numerous organic constituents of wood, and other chemical species produced during the pulping process. The composition of liquor is a very important variable in the overall corrosion of mill equipment exposed to black liquor. However, the composition of black liquor varies from mill to mill, and within one mill with changes in chemical charge, cooking parameters, and species of wood pulped. The major inorganic species in black liquor are sodium sulfide, sulfate, sodium thiosulfate, sodium carbonate, and sodium hydroxide. Sodium chloride is also present as an impurity that may either originate from the water supply and/or the wood chips. Whereas, the organic content of the black liquor largely depends on the wood species pulped and on the cooking process used.

The majority of published work on the effects of inorganic chemical concentrations on corrosion in pulping liquors was done for white and green liquors, where the role of constituents is relatively easy to study in a laboratory. The role of each inorganic species in the white and green liquor has been studied, reported, and reviewed by various researchers [1-6]. A number of studies [7-17] have shown that the corrosion rate in black liquors does not correlate with their inorganic composition. There are clear indications that organic constituents of black liquor play an important role in determining its corrosivity. However, there are literally hundreds of organic compounds detected in black liquors and they vary from wood species to wood species. For birch kraft black liquor, Niemela [18] discovered around 600 compounds but could only identify ~350 organic compounds using gas-liquid chromatography and mass spectrometry (GLC-MS). The role of wood extractives and other organic constituents of black liquor in the corrosion of pulping equipment is not very well understood.

Wensley [13] studied the corrosion behavior of carbon steel in three different liquors, one from a mill pulping hardwood exclusively, and the other two from a mill pulping softwood and hardwood alternately. Based on electrochemical results, it was concluded that the carbon steels exhibit active, passive, and transpassive corrosion behavior in digester liquors, but the potential range for the passive region is very small for the softwood liquors compared to the hardwood liquors. Extraction liquors from softwood species were considerably more aggressive than hardwood extraction liquors. It was also reported that rates of corrosion did not correlate with the inorganic composition of tested liquors. Wood species (organic constituents and byproducts) seemed to have a significant influence on the corrosion behavior of carbon steel in different liquors. Kelly et al. [15] analyzed the corrosivity dependence of various digester liquors on their solids contents, sulfides, sulfates, thiosulfates and chloride concentrations and reported a significant variation in the corrosivity of different liquors. They did not find any correlation between the corrosivity and inorganic constituents of tested black liquors.

The organic species in black liquor contain the degradation products of wood and include a variety of organic acids, fatty acids and aliphatic sulfur compounds (such as dimethylsulfide). In addition to these organics, other wood extractives such as turpenes, resins and phenols are also present. A number of compounds like thujaplicins, catechols, pyrogallol, pinene, taxifolin, which are found in different wood species, have been pointed out as corrosive agents [9, 15-17].

Before the 1950s sulfate pulp-mill operators on the northwestern coast of North America found accelerated digester corrosion when they pulped western red-cedar (*Thuja plicata*) instead of western hemlock (*Tsuga heterophylla*) [9]. In one mill, the indicated life of a digester, used exclusively for pulping western red-cedar, was half the life of other digesters used for western hemlock and Douglas-fir (*Pseudotsuga menziesii*). MacLean and Gardner [9] investigated the role of a few organic species and degradation products in digester corrosion. Results from experimental cooks showed that western red-cedar and Douglas-fir caused rapid attack on mild steel (50 to 60 mils per year) and the black liquor from western red-cedar was 50 to 60% more corrosive than that from Douglas-fir. Western hemlock was reported to be relatively non-corrosive. MacLean and Gardner [9] concluded that the accelerated corrosion during pulping of western red-cedar in the areas which come in contact with the black liquor is caused by the presence of polyphenols of a catechol nature in the black liquors from western red-cedar. MacLean and Gardner [9] suggested that the corrosion in the presence of western red-cedar liquor was due to the phenolic portion of the extractives. They argued that the polyphenols in western red-cedar are derivatives of catechols, and because Douglas-fir contains catechol derivatives (dihydroquercetin) and is also corrosive, therefore, catechol derivatives must be responsible for the corrosion of carbon steels in these black liquors.

It is significant that 1-2-dihydroxybenzene compounds, such as catechol, the 1,2,3-trihydroxybenzene (pyrogallol), and their derivatives, cause active corrosion of carbon steels during alkaline pulping. Derivatives of catechol, e.g., catechin, queracetin, dihydroqueracetin, and derivatives of pyrogallol, e.g., gallic acid, allagic acid, gallotanins, and ellagitannins occur widely in plants and as components of extractives of many pulpwoods and their barks [20]. Relative concentrations of these compounds in a given wood species may affect the relative corrosivity of its black liquor.

Although different di- and trihydroxybenzenes (guaiacol, resocinol, catechol, pyrogallol) increase corrosion potential of steel, the magnitude of the effect depended on their chemical structure and concentration. Pinene, an extractive extensively found in certain softwoods, and pyrogallol, a lignin degradation product are dihydroxybenzene and trihydroxybenzene compounds, respectively, and act as chelates to make complexes with iron. Di- and trihydroxybenzene structures with adjacent hydroxy groups can form complexes with Fe^{+2} ions relatively easily; therefore they have a greater effect on inhibiting passivation of carbon steels and hence increase their corrosion. However, chelation reactions are also sensitive to the pH.

Niemela [19] has identified 14 different catechols in pine kraft liquor. The most abundant compound was catechol (1,2-dihydroxybenzene), which was present in relatively high amounts (60-64 mg/liter) after the heating up period, whereas, only traces of other catechols and their derivatives could be detected after 165 minutes of cooking. Most of the catechols are formed by demethylation of their corresponding guaiacil structures, although the easy liberation of native catechol structures in lignin and aromatization reactions of carbohydrates also contribute to their formation during the pulping process. Investigators have confirmed that catechol and its derivatives can be formed from carbohydrates under alkaline conditions [19]. However, the fragmentation and recombination reactions required for the formation of catechols from carbohydrates are not well understood.

Kannan et al. [17] measured the corrosivity of synthetic black liquor prepared with a set of 23 chemicals on A283 carbon steel samples. The results indicated that sodium sulfite, abietic acid, dimethyl sulfide, pinene, sodium thiosulfate and pyrogallol are the chemicals that most contributed to the corrosion of A283 carbon steel in synthetic liquor. High concentrations of catechols (10g/L) were found to inhibit passivation due to their ability to form metal complexes with iron and their ability to destabilize iron oxides [4, 16].

Certain wood species contain other compounds that are known to increase the corrosivity of black liquors. Heartwood in Eucalyptus species contains appreciable amounts of acids, and the pH values of Eucalyptus wood extracts have been found to be around 2.5 and lower [20]. Although acetic and formic acids are known to be present in the Eucalyptus heartwood, the extent to which they contribute to acidity is not known. These acids are volatile weak acids, and like tropolones, can only cause corrosion in the liquid region of digesters before the chips are covered with alkaline pulping liquor [9, 20]; nevertheless, these acids can participate in the condensed vapor region of digesters or other black liquor handling equipment. However, if wet chips adhere and are isolated on digester walls, then, it may be possible to get local pHs lower than the bulk mixtures.

Corrosivity of black liquors may also be affected by the inhibiting properties of certain organic compounds. Various degradation products of lignin may also inhibit corrosion. Tannin has been reported to form an organo-metallic compound with iron in alkaline solutions [21]. Alkali metal tannates act as corrosion inhibitors for carbon steels [22] and their formation may decrease corrosivity of black liquors. Tannins are also known to protect ferrous alloys from atmospheric as well as underground corrosion [23].

In most published work on corrosivity of black liquors, it is very difficult to separate out the effects of pulping conditions or inorganic constituents of black liquor from the effect of organic constituents on overall corrosivity of black liquors. Direct comparisons are difficult to make as the processing variables were not similar in most studies or have not been reported. The present study was aimed at establishing the relative corrosion susceptibility of carbon steels and other alloys in black liquors from different wood species, which were pulped in white liquor with the same composition under similar cooking conditions, leaving similar amounts of residual inorganic chemicals in resulting black liquors. This is an initial effort in defining the role of different black liquor constituents in overall liquor corrosivity. We tested the performance of five commonly used alloys in black liquors obtained after pulping five different wood species using the kraft process. The composition of the black liquors was analyzed and correlated with the corrosion rates found in different alloys.

EXPERIMENTAL PROCEDURE

Five wood species, commonly used for papermaking, were selected from different regions of the United States. The species scientific name and general location are indicated in Table I.

Table I. Wood species, type and localization region in the U.S.

Common Name	Scientific Name	Type	U.S. Region
Douglas-fir	*Pseudotsuga taxifolia*	Softwood	Northwest
Loblolly pine	*Pinus taeda*	Softwood	Southeast
Cottonwood	*Populus deltoides*	Hardwood	Southeast
Sweetgum	*Liquidambar styraciflua*	Hardwood	South Central
Willow Oak	*Quercus phellos*	Hardwood	South

Wood chips from different species were cooked individually under conventional kraft pulping conditions in a laboratory digester, and the black liquor was extracted. One and a half kilograms of oven-dry chips of a given species was cooked in a white liquor with 25% sulfidity and 18% effective alkali. Liquor to wood ratio was kept to 4:1 for every cook. Pulping conditions were maintained constant for all the cooks. After placing wood chips in the digester, white liquor was added and the temperature was increased from room temperature to 170°C in 90 minutes. The time at maximum temperature was 45 minutes for the hardwoods and 60 minutes for softwoods, which is consistent with industrial practice.

The black liquor was blown out via a condenser from the bottom of the digester. The bottles were filled completely with black liquor under nitrogen gas cover to avoid oxidation, and the liquor was allowed to cool. The bottles were stored in a cold room at 5.5°C (42°F) overnight.

Titration method was used to quantify residual NaOH, Na_2S, and Na_2CO_3 using an industry-standard ABC-procedure [24] and Mettler Toledo titrator. Capillary Ion Electrophoresis (CIE) was used to determine $S_2O_3^{-2}$, Cl^-, and SO_4^{-2} ion concentration as well as low-molecular-weight organic acid content in the liquor. An attempt was also made to detect catechols in the liquor using CIE but was not successful. Each liquor was also analyzed after the corrosion test to characterize any changes in the liquor composition.

Five materials of construction, one carbon steel (A 516-G70), two austenitic stainless steels (SS316, SS304), and two duplex stainless steels (2304, 2205), were selected for this study. These materials are used in the construction of batch and continuous digesters and other black liquor handling equipment throughout the industry. Composition of these alloys is given in Table II. All the specimens were measured to calculate the exposed areas, and the initial weight of each specimen was recorded using an analytical balance. Duplicate coupons were arranged in an insulated rack with a Teflon base. Crevice washers were used to construct these racks. The racks with duplicate metal coupons were placed in a 2205 stainless steel 3-liter autoclave and submerged in the black liquor. The autoclaves were closed and heated with electric jackets and the specimens were exposed in the black liquor at 338°F (170°C) for 15 days, after which the coupons were removed, weighed, and examined for general and localized corrosion under the microscope.

Table II. Chemical composition of alloys used.

Alloy	Al	C	Cr	Cu	Fe	Mn	Mo	N	Ni	P	S	Si	V
A516	0.036	0.230	0.020	0.010	98.28	1.110	0.004	0.003	0.010	0.007	0.010	0.260	0.02
316		0.024	16.29		68.91	1.87	2.12	0.030	10.28	0.030	0.001	0.440	
304L		0.060	18.25	0.410	70.31	1.810	0.320	0.060	8.18	0.028	0.0003	0.570	
2205		0.010	22.45		66.38	1.66	3.19	0.153	5.57	0.024	0.006	0.56	
2304		<0.03	23.0		72.87	-	-	0.10	4.00	-	-	-	

The coupons were thoroughly cleaned with water, dried, and stored individually in closed plastic bags in a dessicator for further quantification. Weight of specimens was recorded before and after cleaning the surface with sandblast. Final weight, after sandblast, was used to calculate the corrosion rate. Before sandblasting, the specimens were examined for localized corrosion attack under crevice washers as well as on the general surface.

Similar tests were also carried out in three synthetic liquors prepared in the laboratory. One of the synthetic liquors (Synthetic-I) was prepared by mixing amounts of inorganic chemicals ($Na_2S_2O_3$, NaOH, and Na_2S) equivalent to the residual inorganics analyzed in the loblolly pine black liquor in the present study. The second synthetic liquor (Synthetic-II) was similar to Synthetic-I liquor but had 0.064 g/L of catechol, which was the amount of catechol identified by Niemela [19] in GLC-MS studies on pine kraft black liquors. The third synthetic liquor (Synthetic-III) was only 5 g/L of catechol in water. This test was done to test the corrosivity of catechol on its own. Synthetic-III had almost three orders of higher concentration of catechol than what was analyzed in pine kraft black liquor by Niemela [19].

RESULTS AND DISCUSSION

Chemical analysis for inorganic composition and analysis for solids content of black liquors were performed before the coupon exposure test, and results are shown in Table III. Residual concentration of Na_2S and NaOH in the black liquors tested was similar for all black liquors tested in this study. Tested black liquors also had similar amounts of $Na_2S_2O_3$ and residual solids in them. Residual concentration of Na_2S and NaOH for all tested black liquors was between 7 and 8% of their initial concentration in the white liquor used for pulping.

Table III. Inorganic Chemicals in Black Liquors before the corrosion test

	Chemical Composition of Black Liquor (in grams/liter)						Solids %
	$Na_2S_2O_3$	Na_2S	NaOH	NaCl	Na_2SO_4	Others	
Loblolly Pine	4.09	6.79	18.75	< 0.202	< 0.202	-	15.6
Douglas-fir	7.00	8.47	20.65	< 0.367	0.49	-	15.4
Douglas-fir-II	7.15	8.47	18.21	< 0.202	0.28	-	15.6
Sweetgum	7.36	10.22	16.72	< 0.204	0.20	-	14.4
Cottonwood	4.57	10.18	17.68	< 0.202	0.32	-	14.1
Willow Oak	8.77	8.47	12.86	< 0.194	0.22	-	17.8
Synthetic-I	4.09	6.79	18.75	0	0	-	-
Synthetic-II	4.09	6.79	18.75	0	0	0.064 - Catechol	-
Synthetic-III	-	-	-	-	-	5.0 - Catechol	-

Results from 15-day coupon exposure tests at 170°C in different black liquors and synthetic liquors are given in Table IV. Corrosion rate for each material, listed in Table IV, is an average value from duplicate test specimens. These results demonstrate that the carbon steel (516-Gr70) experiences significantly higher corrosion rates in corrosive black liquors than the austenitic or duplex stainless steel samples tested in the same liquor.

Table IV. Average Corrosion Rate in mils per year (mpy)

Wood species	Corrosion Rate in mils per year (mpy)				
	A516-Gr 70	**304**	**316**	**2205**	**2304**
Loblolly Pine	78.68	0.25	0.32	0.16	0.10
Douglas-fir-I	83.39	0.27	0.67	0.03	0.08
Douglas-fir-II	87.44	0.05	0.56	0.00	0.00
Sweetgum	0.00	0.10	0.05	0.17	0.11
E. Cottonwood	0.05	0.08	0.01	0.13	0.09
Willow Oak	32.61	0.15	0.06	0.06	0.04
Synthetic I*	0.18	0.12	0.21	0.21	0.14
Synthetic II**	0.30	0.18	0.10	0.03	0.04
Synthetic III***	2.43	0.18	0.10	0.14	0.13

* NaOH, Na_2S, NaS_2O_3; ** NaOH, Na_2S, NaS_2O_3 + 60 mg/L Catechol; *** 5 g/L Catechol

Carbon Steel (A516 -Gr70)

Softwood black liquors

A516-Gr70 coupons in softwood black liquors (loblolly pine and Douglas-fir) showed a very high corrosion rate of around 80 mpy. A black dusty film, which could be easily removed, covered these specimens. Corrosion was uniform and the attack was significantly less severe under the crevice washers compared to the general exposed surface of carbon steel coupons in softwood black liquors as shown in Figure 1. Duplicate tests were conducted for the softwood species where fresh black liquor was used in each experiment and the results for duplicate tests were very reproducible. Douglas-fir chips were pulped in two different batches and tests were conducted to check the reproducibility of our tests and the results shown in Table IV for Douglas-fir-1 and Douglas-fir-II were very similar.

Hardwood black liquors

Carbon steel specimens showed almost negligible corrosion in sweetgum and eastern cottonwood black liquors. These specimens had brownish film on the surface but removal of the film exposed an unattacked surface underneath after 15 days of exposure at 170°C. Whereas, in willow-oak black liquor, which is also a hardwood, the corrosion rate of carbon steel specimens was significantly higher (~ 30 mpy) than that for the sweetgum and eastern cottonwood black liquors. Figure 2 shows carbon steel specimen exposed in willow-oak black liquor showing general corrosion.

Synthetic liquors

Tests were also conducted in the synthetic-liquor (synthetic-I) containing the same amounts of inorganic compounds as were analyzed in the loblolly pine black liquor in the present study. This test was conducted to establish the effect of inorganic species alone on the corrosion of different alloys. Carbon steel specimens showed a black dark film after 15 days of exposure at 170°C but the corrosion rate was very low (~0.2 mpy) compared to the loblolly pine (~80 mpy). A very small amount of localized corrosion was observed under the crevice that could only be detected under an optical microscope. This clearly indicates that the inorganic components of an aggressive black liquor, loblolly pine in the present case, do not explain the overall corrosivity of black liquor.

Previous work by MacLean and Gardner [9] as well as by Kannan et al. [4] has indicated that the catechols in liquor may be the reason for the aggressive nature of certain black liquors. To test that, we exposed specimens to another synthetic liquor (Synthetic-II) which was similar to the Synthetic-I but had catechol in it. The amount of catechol was the same as was analyzed and reported by Niemela [19] in the loblolly pine black liquor (i.e., 0.064 grams/liter). Results in Table IV indicate that the corrosion rate of carbon steel in this liquor is more than that for the liquor without catechol (Synthetic-I). However, the difference is very small and the corrosion rate of carbon steel in Synthetic-II is still very low (~0.4 mpy) compared to that for the loblolly pine black liquor (~80 mpy).

To check the corrosivity of catechols toward selected materials, tests were carried out in synthetic liquor (synthetic-III) which contained 5 grams per liter of catechol in water, as shown in Table III. Corrosion rate results, shown in Table IV, show that the corrosion rates of carbon steel were very low compared to similar tests in softwood black liquors. Catechol concentration used in synthetic-III was three orders higher (5g/L) than in loblolly pine black liquor (0.064 g/L) as reported by Niemela [19]. These results indicate that the catechol alone (even in concentrations much higher than that reported in loblolly pine black liquor), or the inorganic constituents of the black liquor alone, or the two in combination do not explain why the softwood (loblolly pine) black liquor has such a high corrosivity. This clearly indicates that the individual corrosivity of any black liquor depends on more factors than tested in this study. There are indications that it is not just individual components but their interactions with each other that may be an important factor in overall corrosivity of black liquors.

Stainless Steel Specimens

As expected, the general corrosion rates of austenitic as well as duplex stainless steel in all tested black liquors were very low (less than 0.7 mpy) compared to the carbon steels. However, the main objective of including stainless steel specimens in this study was to check localized corrosion susceptibility of different stainless steels in different black liquors. All tested specimens were observed under the optical microscope for localized attack. Table V summarizes these observations.

Softwood Black Liquor

304 and 316 stainless steel coupons tested in the loblolly pine and Douglas-fir black liquor had a yellowish film on the surface. Slight localized corrosion attack was observed under the crevice washers for both austenitic stainless steels tested. 2205 duplex stainless steel specimens showed few corrosion pits on the surface and minor crevice attack under the washers, as shown in Figure 3, but did not show significant uniform corrosion. However, 2304 SS did not show any signs of localized attack in softwood black liquor tests.

In Douglas-fir black liquor, 304 and 316 stainless steel specimens were covered with a dark brown film and exhibited significant crevice corrosion attack under washers for the 304 specimen, as shown in Figure 4. The 304L SS specimen exposed in Douglas-fir black liquor also had corrosion pits on the surface, as shown in Figure 5. 2205 and 2304 duplex stainless steels did not show any signs of localized corrosion attack in two separate tests done in Douglas-fir black liquors.

Hardwood Black Liquor

Austenitic as well as duplex stainless steel specimens had a light yellowish film on the surface; 2205 and 2304 were slightly stained. However there were no signs of crevice corrosion or pitting attack on any of the stainless steel specimens tested in sweetgum or E. cottonwood black liquors.

Table V. Localized attack on different steel alloys.

Wood Species	Type of localized corrosion attack			
	304 SS	**316 SS**	**2205 DSS**	**2304 DSS**
Loblolly Pine	Crevice	Crevice	Crevice/ Pitting	-
Douglas-fir	Crevice/ Pitting	Crevice	-	-
Willow Oak	-	Crevice	-	-
Sweetgum	-	-	-	-
E. Cottonwood	-	-	-	-
Synthetic I	Crevice/ Pitting	Crevice	Crevice	Crevice
Synthetic II	Crevice	Crevice	Crevice/ Pitting	Crevice
Synthetic III	-	-	-	-

Minor crevice corrosion was noticed on 316L specimens tested in willow-oak black liquor as shown in Table V. Willow oak black liquor was also the most corrosive to the carbon steel among hardwood liquors, as shown in Table IV. However, 304L or duplex stainless steel specimens did not show any signs of localized attack in willow-oak black liquor.

Synthetic Liquors

Tests in synthetic-I and II liquors produced a brownish film on the surface of 304 and 316 stainless steel coupons, whereas, duplex stainless steel specimens had a yellowish film on the surface. Crevice corrosion was observed on all stainless steel specimens tested in synthetic-I and synthetic-II liquors. Dispersed pits were also observed on the surface of 2205 duplex stainless steel specimens as shown in Figure 6.

The synthetic-II liquor containing 0.064 g/L of catechol did not appear to be significantly aggressive towards different alloys. Corrosion rates of A516-Gr70 and 304L SS were 0.3 and 0.18 mpy respectively. MacLean and Gardner [9] showed that addition of 4.2 g/L of catechol to a 20 g/L NaOH solution increased the corrosion rate of carbon steel to 48 mpy compared to only 0.5 mpy for the solution without catechol. However, the concentration of catechol in our tests was much lower than that used by MacLean and Gardner. Significantly higher concentrations of catechol were also used in studies by Kannan and Kelly [4] or Tonsi-Eldakar and McGlynn [10,11] compared to the amount of catechol in the synthetic-II liquor used in the present study, which was based on the amount of catechol identified in pine kraft black liquors using GLC-MS studies (60mg/L) [19].

Specimens tested in synthetic-III liquor, which only had 5 g/L of catechol in it, did not show any signs of uniform or localized attack on any stainless steel specimens. These results indicate that catechol in concentrations indicated by Niemela [19] for loblolly pine black liquor alone do not sufficiently explain the higher corrosivity of this softwood black liquor.

Duplex stainless steels (2205 and 2304) with their higher chromium content did not show any sign of localized attack in any of the tested black liquors, except for the minor crevice attack of 2205 duplex stainless steel specimens in loblolly pine black liquor. Whereas, all stainless steel specimens tested in synthetic liquors, synthetic-I and synthetic-II, showed crevice attack as well as dispersed pitting attack on the 2205 SS. Synthetic-I and -II liquors contained the same amounts of inorganics as analyzed in loblolly pine black liquor and were very similar to all other black liquors tested in the present study. This clearly indicates that certain compounds in black liquors protect stainless steels from localized corrosion attack, whereas in softwood and willow oak black liquors there are others which cause higher corrosion rates for the carbon steel specimens. Other major organic constituents of the black liquors should also be investigated systematically to understand the role of individual organics and their collective effect through chemical interactions with one another in determining the overall corrosivity of different black liquors.

CONCLUSIONS

1) Carbon steel specimens exposed to loblolly pine and Douglas-fir (softwoods) black liquors exhibited corrosion at rates higher than 78 mpy.
2) E. cottonwood and sweetgum (hardwood) black liquors did not cause significant corrosion of carbon steel specimens, whereas the black liquor from willow oak, which is also a hardwood, caused carbon steel to corrode at a rate of 33 mpy.

3) Although the concentration of inorganic constituents as well as solids content were similar in five black liquors tested in this study, there was a significant difference in the corrosion rates of carbon steel specimens exposed in these liquors. This clearly indicates that organic constituents play a very important role in the overall corrosivity of black liquors.
4) There is no correlation between the inorganic compounds of black liquor and the corrosion rate on steel alloys.
5) Liquors that cause high corrosivity towards carbon steel (i.e., Douglas-fir, loblolly pine, and willow oak) generally also cause localized attack on 304L and 316 austenitic stainless steels.
6) Duplex stainless steel specimens in general have performed very well in all tested black liquors.
7) Presence of catechol at concentrations of 60mg/L, as was analyzed in loblolly pine kraft black liquor using GLC-MS [19], does not alone account for the high corrosivity of loblolly pine black liquor.
8) Other major organic constituents of the black liquors need to be investigated systematically to understand their individual role as well as their collective effect through chemical interactions with one another in determining the overall corrosivity of different black liquors.

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Figure 1. General corrosion on A516-70 carbon steel specimen exposed to Douglas-fir-II black liquor at 170°C in autoclave.

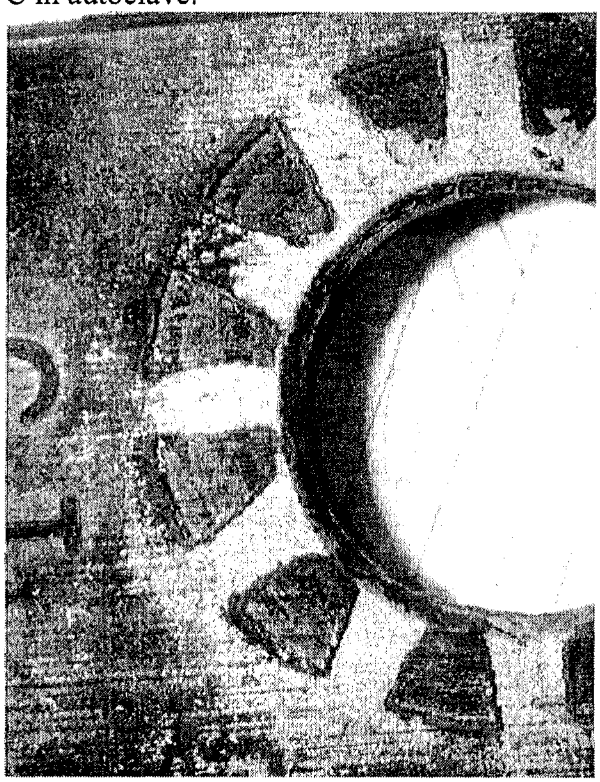

Figure 2. General corrosion on A516-70 carbon steel specimen exposed to willow oak black liquor at 170°C in autoclave.

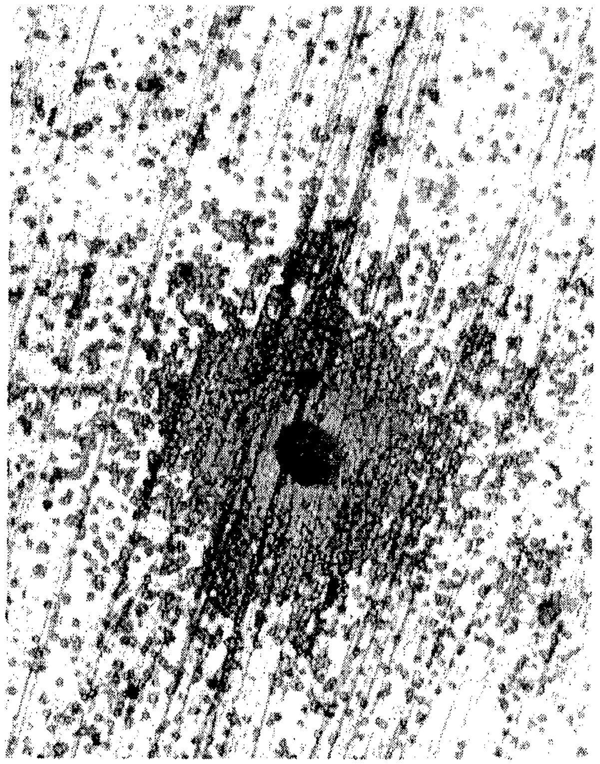

Figure 3. Pitting corrosion on 2205 duplex stainless steel specimen exposed to loblolly pine black liquor at 170°C in autoclave.

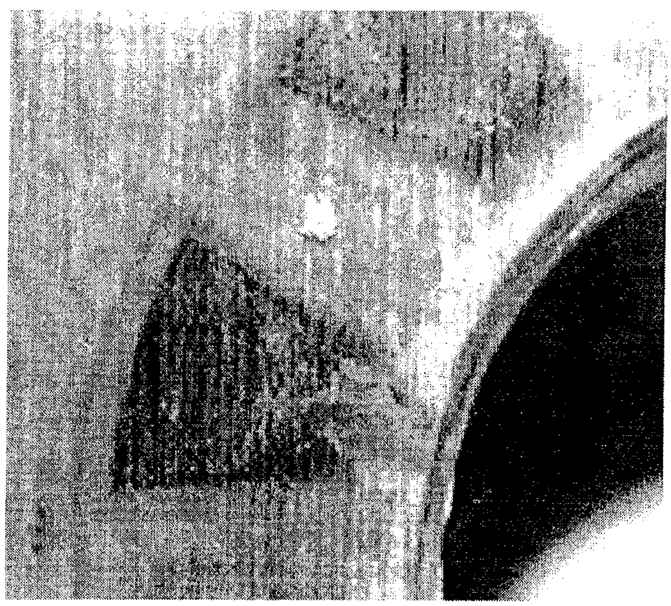

Figure 4. Crevice corrosion on 304L stainless steel specimen exposed to Douglas-fir black liquor at 170°C in autoclave.

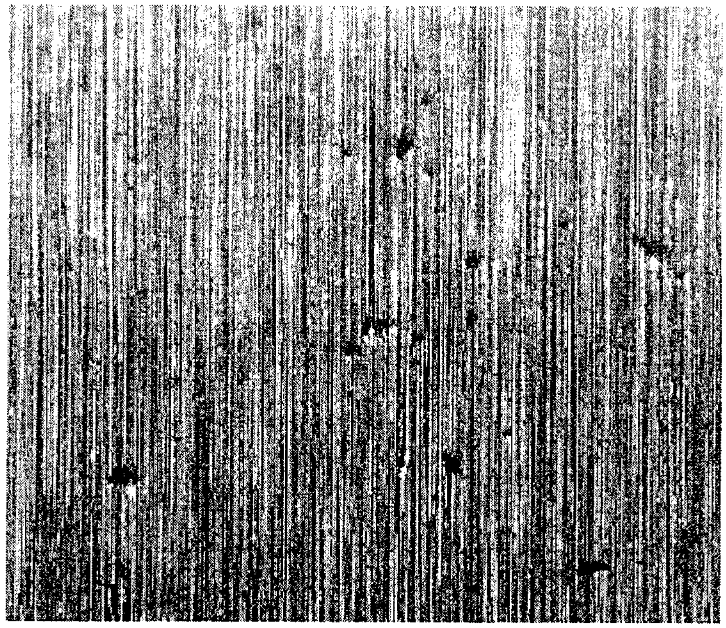

Figure 5. Pitting on surface of 304 stainless steel specimen tested in Douglas-fir black liquor at 170°C.

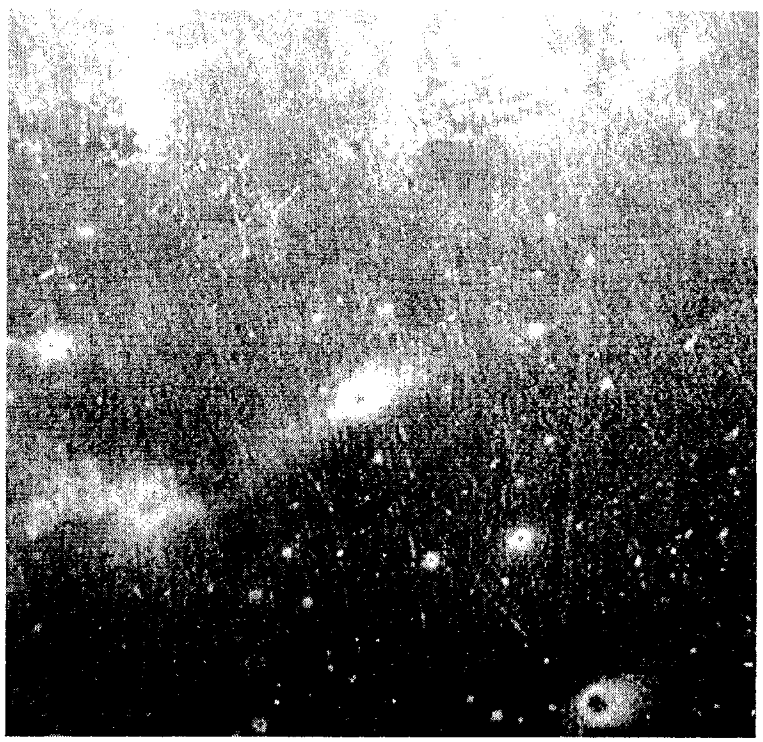

Figure 6. Pitting on surface of 2205 duplex stainless steel specimen tested in synthetic-II liquor at 170°C.